Preparation of organoacyl phosphites

The present invention relates to a process for preparing organoacyl phosphites and optionally organoacyl phosphonites and organoacyl phosphinites which have an organophosphite structural unit, by condensing phosphorus trihalides or organophosphorus halides with a compound which has a salicylic acid group and optionally further compounds bearing hydroxyl groups in the presence of polymeric basic ion exchange resins.

Owing to their broad field of application, organophosphorus compounds have gained considerable industrial importance. They are used, for example, as plasticizers, flame retardants, UV stabilizers and antioxidants. In addition, they constitute important intermediates in the preparation of fungicides, herbicides, insecticides and pharmaceuticals. Accordingly, a large number of preparative processes has been developed. Particularly important among the organophosphorus compounds is the substance class of organophosphites. One review of the preparative methods for organophosphites is by K. Sasse and can be found in "Methoden der Organischen Chemie" [Methods of Organic Chemistry] (Houben-Weyl), Volume XII/2, Chapter 1, Thieme Verlag, Stuttgart (1964) and L. Maier, G. Kosolapoff, "Organic Phosphorus Compounds", Volume 4, John Wiley & Sons, p. 255-462 and the literature references contained therein.

The preparation of triaryl phosphates by reacting phosphorus trihalides with suitable phenols succeeds in the presence of a catalyst in an inert solvent at temperatures of from 150 to 200°C (DE 20 28 878, DE 20 07 070). The hydrogen chloride which is formed is distilled off in situ. This process has a series of disadvantages. In order to bring about the in situ distillation of the hydrogen chloride, high temperatures are necessary. Especially at elevated temperature, hydrogen chloride is extremely corrosive and therefore requires the use of special materials in the plant construction. In addition, the reaction times are very long, which has the consequence of a high fraction of by-products and therefore costly and inconvenient purification of the crude product.

It is therefore often industrially more advantageous to condense phosphorus trihalides, monoaryl dichlorophosphites or halodiaryl chlorophosphites with phenols in the presence of

basic compounds which scavenge the hydrogen chloride being formed. The bases used are usually nitrogen compounds, for instance trialkylamines (DD 301615, US 4,415,686, JP 54030140), dimethylformamide (JP 10053595, EP 511156), N,N-dialkylanilines or nitrogen heterocycles such as pyridine (G. Kosolapoff, "Organophosphorus Compounds", John Wiley &

5   Sons (1950), p. 184). Other processes employ alkali metal and/or alkaline earth metal hydroxides (EP 0032202). JP 54030140 describes the condensation of phosphorus trihalides with phenols in the presence of substoichiometric amounts of amines, ammonium salts, carboxylic acids, guanidines, amides, amidines, sulfones and phosphines.

10   The document WO 91/09040 describes the preparation of sterically hindered triaryl phosphites starting from the corresponding phenols and phosphorus trihalide in the presence of mercaptothiazoles and dithiocarbamic acid derivatives.

WO 03/078444 describes the preparation of compounds having silyl groups as substituents,

15   referred to as phosoxophites, by reacting suitable phosphorus-halogen compounds with a compound having an acid and an OH group in the presence of triethyalmine.

A review of the synthetic methods of organophosphites is given for example, in Houben-Weyl, "Methoden der Organischen Chemie", XII/1, p. 44 ff. A review of the methods for the synthesis

20   of organophosphinites is given in Houben-Weyl, "Methoden der Organischen Chemie", XII/1, p. 210 ff.

One disadvantage of the known industrial processes is the removal of the base and/or its reaction products or the catalysts in the workup of the crude organophosphorus product. A

25   distillative separation is often possible only with difficulty or even impossible as a consequence of the low vapor pressures of the components involved. When a solid base is used and/or the reaction products of the base occur in solid form or a precipitation of the base and/or its reaction products is possible, a removal from the crude product may be effected by filtration or sedimentation. On the industrial scale, especially in a continuous procedure, these separating

30   operations are known to be extremely costly and inconvenient in the industrial construction and operation. They are sensitive toward changes in the operating parameters and/or type and properties of the substances to be separated. In general, it is also necessary to use large amounts

of solvent, for example in order to wash product of value from the filtercake. However, this often succeeds only incompletely (US 5,710,307).

When tertiary amines, especially triethylamine, are used, the trialkylammonium halides which
5   precipitate out lead to a sharp increase in the viscosity of the reaction mixture and to the formation of wall deposits. Under these conditions, stirring and heat exchange are considerably complicated. In order to counter this disadvantage, the document EP 1 234 831 proposes relatively long-chain tertiary amines such as tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine and tri-tert-butylamine. Nevertheless, the fundamental
10   disadvantages of filtration mentioned above remain on the industrial scale.

A further workup of the crude organophosphorus products may be effected by methods known to those skilled in the art, for example by (fractional) crystallization, sublimation, precipitation or chromatographic methods, in some cases also by distillation or rectification. The use of these
15   separating methods on the industrial scale is also associated with a high level of technical complexity and expense.

The document EP 0 285 136 claims a process for purifying tertiary organophosphites to free them of pentavalent organophosphorus compounds which are by-produced in the synthesis or
20   are formed as degradation or hydrolysis products of the tertiary organophosphites. The process envisages a treatment of the dissolved impure organophosphite with water at elevated temperature in the presence of a Lewis base. The Lewis bases used are inorganic salts (carbonates, hydroxides, oxides), tertiary amines and polymers which bear amine groups.

25   However, the synthesis of the organophosphorus compounds itself is not addressed. One disadvantage of the claimed process is in the treatment with water. Not only the impurities to be removed but also the tertiary organophosphites, especially (organo)chlorophosphites, themselves react under the given conditions, so that, depending on the hydrolysis stability of the organophosphites, a portion of the product of value is lost.
30

DE 100 53 272 describes the preparation of diphosphites in which one phosphite unit has a salicylic acid building block. DE 100 58 383 describes the preparation of phosphinines which

have at least two phosphorus atoms. DE 101 14 868 describes the preparation of diphosphines. DE 101 40 083 and DE 101 40 072 describe the preparation of diphosphites in which both phosphite units have a salicylic acid building block. DE 101 400 86 describes the preparation of monophosphites which have a salicylic acid building block. DE 102 10 918 describes the

5 preparation of diphosphites in which at least one phosphite likewise has a salicylic acid building block. All of the aforementioned documents describe the use of tertiary amines, especially of triethylamine, pyridine or N-methylpyrrolidinone, in the reaction of phosphorus halides with alcohols.

10 The existing processes have one or more of the following disadvantages:

a) The complete removal of the base used from the target product is costly and inconvenient.

b) The salts, formed in the reaction, of the bases used are frequently voluminous or occur in a particle size distribution which complicates the removal by filtration.

c) The maintenance of the desired reaction temperature is difficult owing to the high

15 exothermicity.

It is therefore an object of the present invention to provide a simple process for preparing trivalent organophosphorus compounds which does not have one or more of these disadvantages.

20

It has been found that, surprisingly, this object can be achieved by preparing trivalent organic phosphorus compounds which have at least one P-O bond by reacting a trivalent phosphorus compound in which at least one halogen atom is bonded to the phosphorus atom with an organic compound which has at least one OH group in the presence of an ion exchange resin.

25 Even though the base is present in heterogeneous phase, sufficient scavenging of the hydrogn halide released is surprisingly achieved.
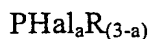
The present invention therefore provides a process for preparing trivalent organophosphorus compounds which bear at least one structural unit S
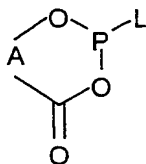
(S)

where A is a divalent substituted or unsubstituted alkyl or aryl radical which may form a ring

system as per structural unit S, and the L radical is an organic radical bonded to the phosphorus

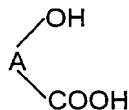atom via an oxygen or carbon atom, or is a halide,

5   by condensing phosphorus compounds of the formula i

$$PHal_aR_{(3-a)} \qquad (i)$$

where Hal is halide selected from chloride, bromide and iodide, and the halides may be the

same or different, R is an organic radical bonded to the phosphorus via a carbon or oxygen

atom, and a = 2 or 3,

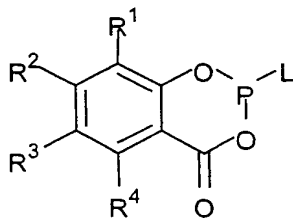10   with an organic compound of the formula S'

(S')

where A is as defined for the structural unit S,

which comprises

carrying out the reaction in the presence of at least one basic ion exchange resin.

15

In particular, the present invention provides a process for preparing trivalent organophosphorus

compounds which have at least one structural unit T

(T)

where R^1, R^2, R^3, and R^4 are each independently selected from monovalent substituted and
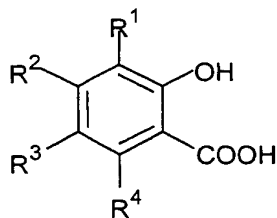
unsubstituted aliphatic, alicyclic, aromatic, heteroaromatic, mixed aliphatic-alicyclic, mixed aliphatic-aromatic, heterocyclic, mixed aliphatic-heterocyclic hydrocarbon radicals having from 1 to 50 carbon atoms, H, F, Cl, Br, I, $-CF_3$, $-CH_2(CF_2)_jCF_3$ with $j = 0 - 9$, $-OR^9$, $-COR^9$, $-CO_2R^9$, $-CO_2M$, $-SR^9$, $-SO_2R^9$, $-SOR^9$, $-SO_3R^9$, $-SO_3M$, $-SO_2NR^9R^{10}$, $-NR^9R^{10}$, $-N=CR^9R^{10}$,

5 where R^9 and R^{10} are each independently selected from H, monovalent substituted and unsubstituted aliphatic and aromatic hydrocarbon radicals having from 1 to 25 carbon atoms, and M is an alkali metal ion, formally half an alkaline earth metal ion, ammonium ion or phosphonium ion, or adjacent R^1 to R^4 radicals together form a fused substituted or unsubstituted aromatic, heteroaromatic, aliphatic, mixed aromatic-aliphatic or mixed

10 heteroaromatic-aliphatic ring system; and the substituted hydrocarbon radicals may have as substituents those selected from $-N(R^5)_2$, $-NHR^5$, $-NH_2$, fluorine, chlorine, bromine, iodine, $-OH$, $-CN$, $-C(O)-R^5$, $-C(O)H$ or $-C(O)O-R^5$, $-CF_3$, $-O-R^5$, $-C(O)N-R^5$, $-OC(O)-R^5$ and/or $-Si(R^5)_3$, where R^5 is a monovalent hydrocarbon radical preferably having from 1 to 20 carbon atoms, and, when a plurality of hydrocarbon radicals R^5 is present, they may be the same or

15 different, and R^1, R^2, R^3 and R^4 radicals may be the same or different, and L is an organic radical bonded to the phosphorus atom via an oxygen or carbon atom, or is a halide, by condensing phosphorus compounds of the formula i

$PHal_aR_{(3-a)}$ (i)

20

where Hal is halide selected from chlorine, bromine and iodine, and the halides may be the same or different, R is an organic radical bonded to the phosphorus via a carbon or oxygen atom and $a = 2$ or 3,

with an organic compound of the formula T'

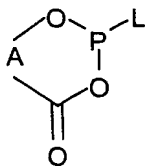25   (T')

where the R^1 to R^4 radicals are each as defined for the structural unit T, which comprises carrrying out the reaction in the presence of at least one basic ion exchange resin.

The process according to the invention has the following advantages over the conventional processes:

a) There are no saltlike by-products which can only be removed with difficulty from the target
5   product.

b) The base used is in solid form and, despite reaction with the hydrogen halide, does not
        change its state of matter and substantially retains its size. The ion exchanger of the process
        according to the invention, typically present as a packing or beads, can be removed from the
        reaction mixture by the simplest means, for example by using coarse-mesh sieves adapted
10   to the size of the ion exchanger particles.

c) Adhesion of large amounts of product of value is prevented by the size and shape of the
        ion exchanger alone. The use of packings or particles of relatively large particle size makes
        the surface of the ion exchanger small relative to the volume compared to a precipitated
        base of the conventional type. Therefore, it is also only necessary to use small amounts of
15   solvent in the process according to the invention in order to flush any adhering product of
        value off the surface of the consumed base.

d) When ion exchanger is used, the rate constant of the reaction is lower than when
        homogeneously dissolved bases are used. As a result, the exothermic reaction becomes
        easy to control.

20 e) during the reaction, no voluminous salts which, as a consequence of the rise in viscosity
        that they bring about, could cause concentration and temperature differences in the reaction
        mixture are formed.

The process according to the invention is described by way of example herein below without
25 the invention being restricted to these embodiments. Further variants which likewise form part
of the subject matter of the present invention and whose field of application is evident from the
description and the claims are evident to those skilled in the art.

In the process according to the invention for preparing trivalent organophosphorus compounds
30 which bear at least one structural unit S

$$\text{A}\begin{array}{c} \diagdown \text{O} \diagdown \\ \\ \diagdown \end{array}\begin{array}{c} \text{P} \diagdown \text{L} \\ | \\ \text{O} \end{array}$$
$$\begin{array}{c} \| \\ \text{O} \end{array}$$

(S)

where A is a divalent substituted or unsubstituted alkyl or aryl radical which may form a ring

system as per structural unit S, and the L radical is an organic radical bonded to the phosphorus

atom via an oxygen or carbon atom, or is a halide,

5   by condensing phosphorus compounds of the formula i

$$PHal_aR_{(3-a)}$$ (i)

where Hal is halide selected from chlorine, bromine and iodine, and the halides may be the

same or different, R is an organic radical bonded to the phosphorus via a carbon or oxygen

atom, and a = 2 or 3,

10   with an organic compound of the formula S‘

$$\text{A}\begin{array}{c} \diagup \text{OH} \\ \\ \diagdown \text{COOH} \end{array}$$

(S‘)
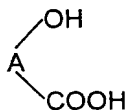
where A is as defined for the structural unit S,

the reaction is carried out in the presence of at least one basic ion exchange resin, preferably an

ion exchange resin present in the form of the free amines (i.e. not present in the OH form).
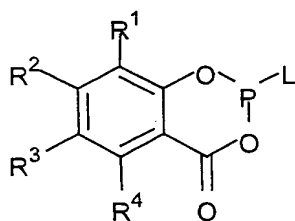
15

When the A radical is an aryl radical, it is preferably bonded to the radical of the structural unit

S via two adjacent bonds (for example 1,2-aryl or 2,3-aryl), in such a way that the structural

unit S has a ring having 6 atoms (a phosphorus atom, 2 oxygen atoms and 3 carbon atoms).

When the divalent A radical of the structural unit S is an alkyl radical, it has, in the chain which

20   is joined to the structural unit at both ends, preferably from 1 to 3, more preferably 1 or 2,

carbon atoms. The A radical may have further carbon atoms, preferably from 1 to 20 carbon

atoms, which are bonded to the carbon atom or atoms of the chain in the case of an alkyl

radical or to the carbon atoms of the aryl radical which are not joined to the sturctural unit S. In

addition to pure hydrocarbon radicals as substituents, the A radicals may also have further substituents, with the proviso that the substituents do not influence the properties, especially with regard to the effectiveness as a ligand. Possible substituents may be selected, for example, from the halogens, nitro, cyano, alkoxy, ether and alcohol groups. Typical A radicals may be,

5 for example, $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, 1,2-phenylene ($-C_6H_4-$), 1,2-naphthylene ($-C_{10}H_6-$), 2,3-naphthylene, 3,5-dichloro-1,2-phenylene, 3,5-dibromo-1,2-phenylene, 3-iodo-5-methyl-1,2-phenylene, 3,5-diisopropyl-1,2-phenylene, 3,5,6-trichloro-1,2-phenylene, 3-phenyl-1,2-phenylene, 1,1-diethyl-1,1-methylene, 1,1-cyclohexylidene, 1,1-cycloheptylidene, 3-isopropyl-6-methyl-1,2-phenylene and similar radicals. The A radical is preferably selected

10 from 1,1-alkylene, 1,2-alkylene, 1,2-phenylene, 1,2-naphthylene and 2,3-naphthylene as divalent radicals or substituted derivatives thereof, in particular halogen- or alkyl-substituted derivatives.

The process according to the invention is particularly suitable for preparing trivalent

15 organophosphorus compounds which have at least one structrual unit **T**

(T)

where R^1, R^2, R^3, and R^4 are each independently selected from monovalent substituted and unsubstituted aliphatic, alicyclic, aromatic, heteroaromatic, mixed aliphatic-alicyclic, mixed aliphatic-aromatic, heterocyclic, mixed aliphatic-heterocyclic hydrocarbon radicals having from

20 1 to 50 carbon atoms, H, F, Cl, Br, I, $-CF_3$, $-CH_2(CF_2)_jCF_3$ with $j = 0 - 9$, $-OR^9$, $-COR^9$, $-CO_2R^9$, $-CO_2M$, $-SR^9$, $-SO_2R^9$, $-SOR^9$, $-SO_3R^9$, $-SO_3M$, $-SO_2NR^9R^{10}$, $-NR^9R^{10}$, $-N=CR^9R^{10}$, $-SiR^9R^{10}R^{11}$ where R^9 and R^{10} are each independently selected from H, monovalent substituted and unsubstituted aliphatic and aromatic hydrocarbon radicals having from 1 to 25 carbon atoms, and M is an alkali metal ion, formally half an alkaline earth metal ion, ammonium ion or

25 phosphonium ion, or adjacent R^1 to R^4 radicals together form a fused substituted or unsubstituted aromatic, heteroaromatic, aliphatic, mixed aromatic-aliphatic or mixed heteroaromatic-aliphatic ring system; and the substituted hydrocarbon radicals may have as

substituents those selected from $-N(R^5)_2$, $-NHR^5$, $-NH_2$, fluorine, chlorine, bromine, iodine, $-OH$, $-CN$, $-C(O)-R^5$, $-C(O)H$ or $-C(O)O-R^5$, $-CF_3$, $-O-R^5$, $-C(O)N-R^5$, $-OC(O)-R^5$ and/or $-Si(R^5)_3$, where R^5 is a monovalent hydrocarbon radical preferably having from 1 to 20 carbon atoms, for example an alkyl radical, in particular methyl, ethyl, propyl or tert-butyl radical, a cycloalkyl radical, in particular cyclopentyl or cyclhexyl radical, or an aryl radical, in particular phenyl or naphthyl radical, and, when a plurality of hydrocarbon radicals R^5 is present, they may be the same or different, and R^1, R^2, R^3 and R^4 radicals may be the same or different, and L is an organic radical bonded to the phosphorus atom via an oxygen or carbon atom, or is a halide,

by condensing phosphorus compounds of the formula i

$$PHal_aR_{(3-a)} \qquad \textbf{(i)}$$

where Hal is halide selected from chlorine, bromine and iodine, and the halides may be the same or different, R is an organic radical bonded to the phosphorus via a carbon or oxygen atom and a = 2 or 3,

with an organic compound of the formula T'

(T')
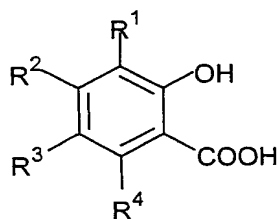
where the R^1 to R^4 radicals are each as defined for the structural unit **T**.

The process according to the invention will be described hereinbelow usually, by way of example, with reference to compounds which have the structural element **T** as a specific form of the structural element **S** without the invention being restricted to the structural element **T**.

The halide Hal in the phosphorus compounds i is preferably chlorine. The R^1 and R^2, R^2 and R^3, or R^3 and R^4 radicals may in particular be benzofused. Nonbenzofused R^1 to R^4 radicals may in particular be primary, secondary or tertiary alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, amyl, sec-amyl, t-amyl, 2-ethylhexyl, iso-nonyl, alicyclic groups such as cyclohexyl, methylcyclohexyl or cyclooctyl, or aromatic groups such as phenyl, naphthyl, tolyl or xylyl. The organic R or L radical may in particular be a W radical which may
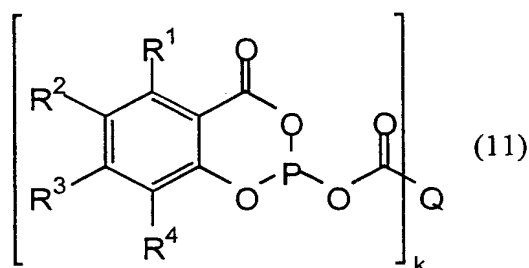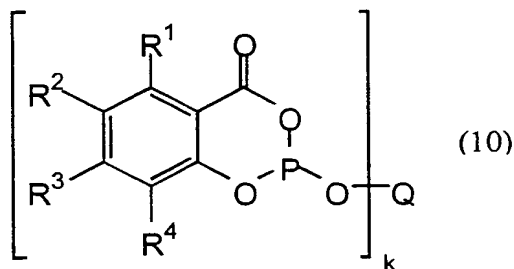
be a substituted or unsubstituted aliphatic, alicyclic, aliphatic-alicyclic, heterocyclic, aliphatic-heterocyclic, aromatic-aromatic or aliphatic-aromatic hydrocarbon radical having from 1 to 50 carbon atoms, and the substituted hydrocarbon radicals may have as substituents those selected from $-N(R^5)_2$, $-NHR^5$, $-NH_2$, fluorine, chlorine, bromine, iodine, $-OH$, $-CN$, $-C(O)-R^5$, $-C(O)H$

5   or $-C(O)O-R^5$, $-CF_3$, $-O-R^5$, $-C(O)N-R^5$, $-OC(O)-R^5$ and/or $-Si(R^5)_3$, where R^5 is a monovalent hydrocarbon radical preferably having from 1 to 20 carbon atoms, and, when a plurality of hydrocarbon radicals R^5 is present, they may be the same or different, or is an organic radical as defined for the W radical which has at least one substituted or unsubstituted phosphite, phosphonite, phosphinite and/or acylphospite radical, and substituents may be selected from

10   those defined for the W radical. The substituents are preferably restricted to those which have no influence on the reaction itself. Particularly preferred substituents for the organic R or L radicals may be selected from the halogens, for example chlorine, bromine and iodine, the alkyl radicals, for example methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, t-butyl, neopentyl, sec-amyl, t-amyl, isooctyl, t-octyl, 2-ethylhexyl, isononyl, isodecyl and octadecyl, the aryl radicals,

15   for example phenyl, naphthyl and anthracyl, the alkylaryl radicals, for example tolyl, xylyl, dimethylphenyl, diethylphenyl, trimethylphenyl, triethylphenyl and p-alkylphenyl, the aralkyl radicals, for example benzyl and phenylethyl, the alicyclic radicals, for example cyclopentyl, cyclohexyl, cyclooctyl, cyclohexylethyl and 1-methylcyclohexyl, the alkoxy radicals, for example methoxy, ethoxy, propoxy, butoxy and pentoxy, the aryloxy radicals, for example

20   phenoxy and naphthoxy, $-OC(O)R^5$ or $-C(O)R^5$, where R5 is a monovalent hydrocarbon radical, for example acetyl, propionyl, trimethylacetoxy, triethylacetoxy and triphenylacetoxy, and the silyl radicals $-Si(R)_3$ having three hydrocarbon radicals, for example trimethylsilyl, triethylsilyl or triphenylsilyl.

25   When the compounds used in the process according to the invention have amine groups, i.e. $-NH_2$, $-N(R^5)_2$ or $-N(alkyl)_2$ or $-NH(alkyl)$ or $-NHR^5$, they have to function as a weaker base relative to the amine groups of the ion exchanger in equilibrium reactions. Compounds which have amine groups and cannot fulfill this condition cannot be used (directly) as reactants in the process according to the invention. One possibility of still using such compounds is to protect

30   the appropriate groups by the incorporation of protective groups in a known manner, and, after carrying out the process according to the invention, remove the protective group again.

The trivalent organophosphorus compounds prepared by means of the process according to the invention may preferably be those which are selected from the compounds of the following formulae

(1 9)

(2 0)

5   (2 1)
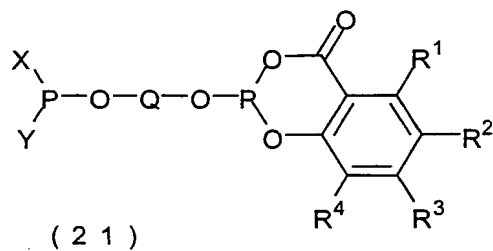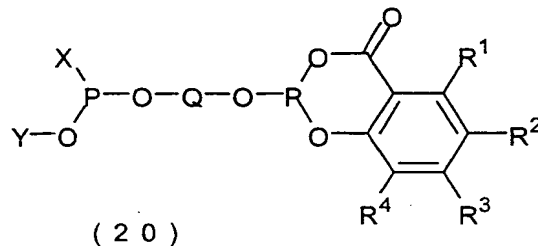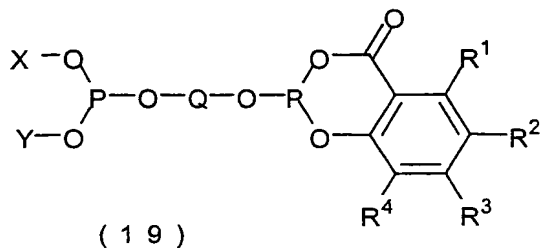
where X and Y are each substituted or unsubstituted, aliphatic, alicyclic, aliphatic-alicyclic, heterocyclic, aliphatic-heterocyclic, aromatic-aromatic or aliphatic-aromatic hydrocarbon radicals having from 1 to 50 carbon atoms, where X and Y are the same or different or

10   covalently joined together, and where Q is an at least divalent, substituted or unsubstituted, aliphatic, alicyclic, aliphatic-alicyclic, heterocyclic, aliphatic-heterocyclic, aromatic, aromatic-aromatic or aliphatic-aromatic hydrocarbon radical, and the substituted hydrocarbon radicals may contain as substituents those selected from $-N(R^5)_2$, $-NHR^5$, $-NH_2$, fluorine, chlorine, bromine, iodine, -OH, -CN, $-C(O)-R^5$, -C(O)H or $-C(O)O-R^5$, $-CF_3$, $-O-R^5$, $-C(O)N-R^5$, -

15    $OC(O)-R^5$ and/or $-Si(R^5)_3$, where R^5 is a monovalent hydrocarbon radical preferably having from 1 to 20 carbon atoms, and, when a plurality of hydrocarbon radicals R^5 is present, they may be the same or different, and where R^1 to R^4 may each be as defined above. The substituents are preferably restricted to those which have no influence on the reaction itself. Particularly preferred substituents may be selected from the preferred substituents specified for

20   R and L.

The trivalent organophosphorus compounds prepared by the process according to the invention may equally possibly be phosphites of the formula 10 or 11

$$(10)$$

$$(11)$$

where R^1, R^2, R^3, and R^4 are each as defined above, Q is a k-valent substituted or unsubstituted, aliphatic, alicyclic, mixed aliphatic-alicyclic, heterocyclic, mixed aliphatic-heterocyclic, aromatic, heteroaromatic, mixed aliphatic-aromatic hydrocarbon radical having from 1 to 50 carbon atoms, and aliphatic moieties of Q may contain oxygen, sulfur and/or nitrogen, and the substituted hydrocarbon radicals may have as substituents those selected from -N(R^5)$_2$, -NHR^5, -NH$_2$, fluorine, chlorine, bromine, iodine, -OH, -CN, -C(O)-R^5, -C(O)H or -C(O)O-R^5, -CF$_3$, -O-R^5, -C(O)N-R^5, -OC(O)-R^5 and/or -Si(R^5)$_3$, where R^5 is a monovalent hydrocarbon radical preferably having from 1 to 20 carbon atoms, and, when a plurality of hydrocarbon radicals R^5 is present, they may be the same or different, k is at least 2, and R^1, R^2, R^3 and R^4 in the individual structural elements T bonded to Q may in each case be defined identically or differently. The substituents are preferably restricted to those which have no influence on the reaction itself. Particularly preferred substituents may be selected from the preferred substituents specified for R and L.

It is equally possible by the process according to the invention to prepare the compounds described in WO 03/078444 and referred to as phosoxophites.

Bisphosphites of the structure **19** are preferably prepared by condensing at least di-OH-substituted hydrocarbons Q' where Q' is a substituted or unsubstituted aliphatic, alicyclic, mixed aliphatic-alicyclic, heterocyclic, mixed aliphatic-heterocyclic, aromatic, heteroaromatic, mixed aliphatic-aromatic hydrocarbon having from 1 to 50 carbon atoms, and aliphatic

moieties of Q' may contain oxygen, sulfur and/or nitrogen, and the substituted hydrocarbons may have as substituents those selected from $-N(R^5)_2$, $-NHR^5$, $-NH_2$, fluorine, chlorine, bromine, iodine, -OH, -CN, $-C(O)-R^5$, -C(O)H or $-C(O)O-R^5$, $-CF_3$, $-O-R^5$, $-C(O)N-R^5$, -OC(O)-R^5$ and/or $-Si(R^5)_3$, where R^5 is a monovalent hydrocarbon radical preferably having

5   from 1 to 20 carbon atoms, and, when a plurality of hydrocarbon radicals R^5 is present, they may be the same or different, with diorganohalophosphites **2** and salicylic phosphorus halide derivatives **T** where L = Hal in the presence of one or more basic ion exchange resins. The substituents are preferably restricted to those which have no influence on the reaction itself. Particularly preferred substituents for Q' may be selected from the preferred substituents
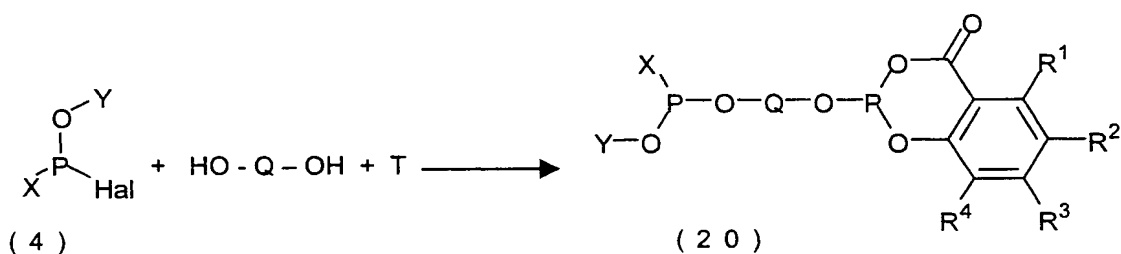
10   specified for R and L.
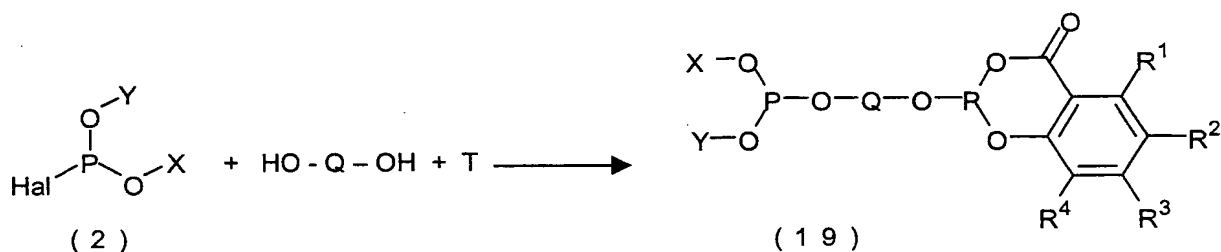
Phosphite-phosphonite compounds of the structure **20** are prepared by means of the process according to the invention preferably by condensing di-OH-substituted hydrocarbons Q' with

15   haloorganophosphonites **4** and salicylic phosphorus halide derivatives **T** where L = Hal in the presence of one of more basic ion exchange resins.


Phosphite-phosphinite compounds of the structure **21** are prepared by means of the process

20   according to the invention preferably by condensing di-OH-substituted hydrocarbons Q' with haloorganophosphinites **9** and salicylic phosphorus halide derivatives **T** where L = Hal in the presence of one or more basic ion exchange resins.
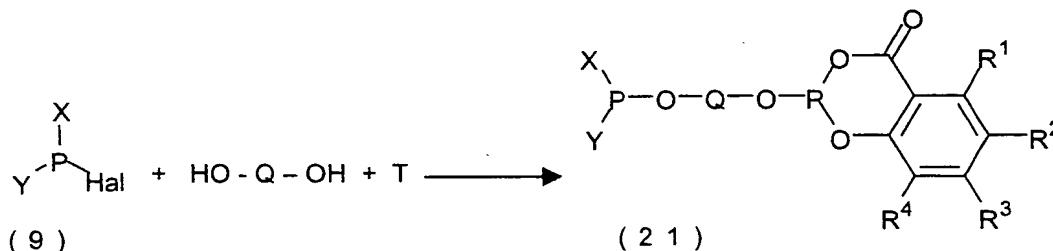
In the formulae **19** to **21**, X and Y may each be as defined above. The hydrocarbons Q' have at least two OH groups. The hydrocarbons Q' having two OH groups are preferably compounds selected from the substituted or unsubstituted compounds 1,4-dihydroxybenzene, 1,2-dihydroxybenzene, 1,8-dihydroxynaphthalene, 1,1'-binaphthyl-2,2'-diol or 2,2'-binaphtyl-1,1'-diol.

The phosphorus compound of the formula i used is preferably at least one compound selected from the compounds of the following formulae:
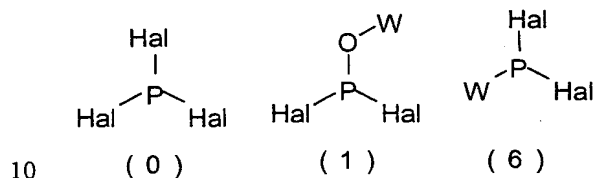
where W is an organic radical as defined above. The phosphorus compound of the formula i used may in particular be a compound of the formula **1** which is prepared by reacting a compound **0** with an organic compound W' having at least one hydroxyl group, preferably likewise in the presence of a basic ion exchanger. The compounds W' having at least one hydroxyl group used may be a substituted or unsubstituted compound having an OH group, for example selected from methanol, ethanol, n-propanol, isopropanol, 1-butanol, 2-butanol, t-butanol, 2-ethylhexanol, isononanol, isodecanol, isotridecanol, phenol, phenol derivatives, or compounds Q' having two or more OH groups, for example selected from 1,4-dihydroxybenzene, 1,2-dihydroxybenzene, 1,8-dihydroxynaphthalene, 1,1'-binaphtyl-2,2'-diol, 2,2'-binaphtyl-1,1'-diol, di- or polyols, for example glycol or sugars, for example cyclodextrins, or the compounds denoted by formula VII in WO 03/078444 or compounds having two or more carboxylic acid groups or a compound which has one or more OH groups and may have one or more of the structural units T, and the substituted compounds may have substituents selected from primary, secondary and tertiary alkyl groups, alicyclic groups, aromatic groups, $-N(R^5)_2$, $-NHR^5$, $-NH_2$, fluorine, chlorine, bromine, iodine, $-CN$, $-C(O)-R^5$,

-C(O)H or -C(O)O-R^5, -CF_3, -O-R^5, -C(O)N-R^5, -OC(O)-R^5 and/or -Si(R^5)$_3$, where R^5 is a monovalent hydrocarbon radical preferably having from 1 to 20 carbon atoms, and, when a plurality of hydrocarbon radicals R^5 is present, they be the same or different. The substituents are in turn restricted to those which have no influence on the reaction itself. Particularly

5   preferred substituents may be selected from the preferred substituents specified for R and L.
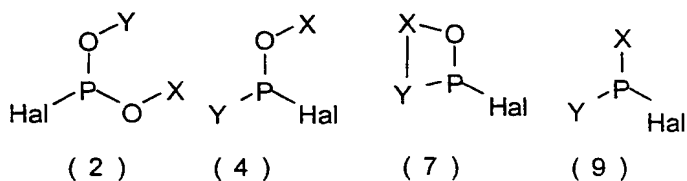
It may be particularly advantageous when the compound having at least one hydroxyl group used is a compound which originally has at least two hydroxyl groups and is obtained by reacting at least one of these groups with a compound of the formula 0 and a compound of the

10   formula T' or an aromatic compound which has two adjacent hydroxyl groups on the aromatic ring. In this way, the compounds of the formulae 10 and 11 and also specific compounds of the formula 19 in which X and Y are joined covalently (in an aromatic ring system) in particular are obtainable.

To prepare compounds of the formula 1, preference is given in each case to initially charging

15   the phosphorus compound together with one or more basic ion exchange resins and subsequently metering in the compound having at least one OH group. It is also possible to initially charge the compound having an OH group together with the ion exchanger and add the phosphorus compound dropwise.

20   In the preparation of asymmetric diphosphorus compounds of the formula 10, 11, 19, 20, and 21 it has been found to be advantageous when the compound having OH groups is initially charged together with one or more basic ion exchange resins and one or more phosphorus compounds are subsequently metered in.

25   In the preparation of symmetric diphosphorus compounds of the formulae 10 and 11, either the compound having OH groups or the phosphorus compound may be initially charged together with the ion exchanger and the other compound accordingly metered in.
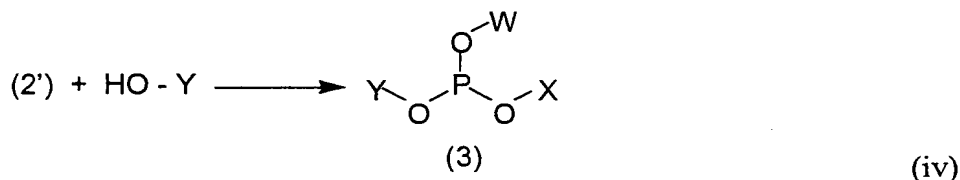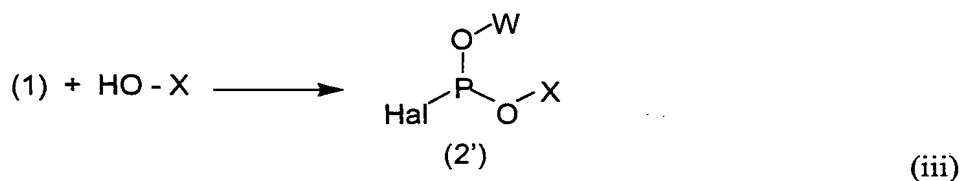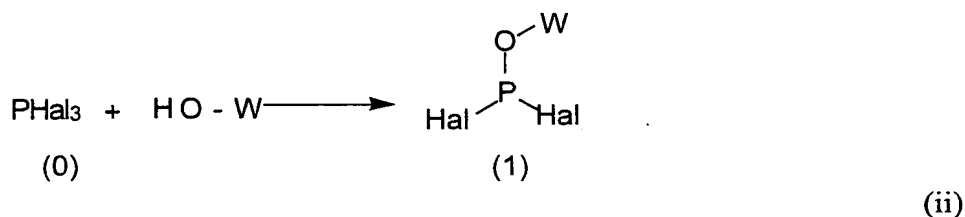
To prepare the compounds 19, 20 and 21, it may be advantageous when a compound selected

30   from the compounds of the following formulae

$$\underset{(2)}{\text{Hal}-\overset{\overset{\displaystyle O^{-Y}}{|}}{P}\overset{\displaystyle O^{-X}}{}} \qquad \underset{(4)}{Y-\overset{\overset{\displaystyle O^{-X}}{|}}{P}-\text{Hal}} \qquad \underset{(7)}{Y-\overset{\overset{\displaystyle X^{-}O}{|}}{P}-\text{Hal}} \qquad \underset{(9)}{Y-\overset{\overset{\displaystyle X}{|}}{P}\text{Hal}}$$

where Hal is halide, Y and X are substituted or unsubstituted, aliphatic, alicyclic, aliphatic-alicyclic, heterocyclic, aliphatic-heterocyclic, aromatic-aromatic or aliphatic-aromatic,

5   hydrocarbon radicals having from 1 to 50 carbon atoms, and X and Y may be the same or different or be covalently joined together, is reacted with a compound Q' having at least two hydroxyl groups, preferably in the presence of a basic ion exchanger. The substituted hydrocarbons may have one or more substituents selected from primary, secondary and tertiary alkyl groups, alicyclic groups, aromatic groups, $-N(R^5)_2$, $-NHR^5$, $-NH_2$, fluorine, chlorine,

10   bromine, iodine, -CN, $-C(O)-R^5$, -C(O)H or $-C(O)O-R^5$, $-CF_3$, $-O-R^5$, $-C(O)N-R^5$, $-OC(O)-R^5$ and/or $-Si(R^5)_3$, where R^5 is a monovalent hydrocarbon radical having preferably from 1 to 20 carbon atoms, and, when a plurality of hydrocarbon radicals R^5 is present, they may be the same or different. The substituents are in turn preferably restricted to those which have no influence on the reaction itself. Particularly preferred substituents for X and Y may be selected

15   from the preferred substituents specified for R and L. The product which is obtained from this reaction and has at least one hydroxyl group is either reacted directly with a compound which has the structural unit **T** (specific type of the compound S) in which L is Hal, or initially with a compound 0 and subsequently with a compound T'. Preference is given to carrying out all of these reactions in the process according to the invention in the presence of a basic ion

20   exchanger.

According to K. Sasse in "Methoden der Organischen Chemie" (Houben-Weyl), Volume XII/2, Chapter 1, p. 62 ff., Thieme Verlag, Stuttgart (1964) and G. M. Kosolapoff, "Organophosphorus Compounds", chap. 7, XV, pp. 139, John Wiley, New York (1950) and the

25   literature references contained therein, the preparation of asymmetric organophosphites and asymmetric phosphonites succeeds by stepwise reaction of the organophosphorus halides or phosphorus halides used as starting substances with compounds containing hydroxyl groups in the presence of amines. Depending on the desired target compound, the process according to the invention may comprise one or more reaction steps, and the reaction of in each case one
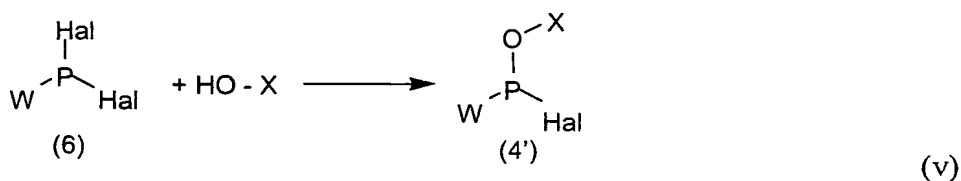
phosphorus-halogen bond with one hydroxyl group is one reaction step. Accordingly, the process according to the invention may be performed as a multistage process for preparing asymmetric organophosphites and asymmetric phosphonites, in which case the reaction steps are each carried out in the presence of a (weakly) basic ion exchanger. The generally possible reaction steps are detailed in the following reaction schemes:

$$PHal_3 + HO-W \longrightarrow \underset{(1)}{\overset{O^{\nearrow W}}{\underset{Hal}{\overset{|}{P}}}} \quad (ii)$$

(0)

$$(1) + HO-X \longrightarrow \underset{(2')}{\overset{O^{\nearrow W}}{\underset{Hal}{\overset{|}{P}}}O^{\nearrow X}} \quad (iii)$$

$$(2') + HO-Y \longrightarrow Y_{\searrow O}\overset{O^{\nearrow W}}{\underset{(3)}{\overset{|}{P}}}O^{\nearrow X} \quad (iv)$$

As illustrated in the formulae **ii**, **iii** and **iv**, it is possible, starting from a phosphorus trihalide, by reacting with one equivalent of a compound containing one hydroxyl group HO-W, to prepare an organophosphorus dihalide, by reacting the organophosphorus dihalide with a further equivalent of a compound containing one hydroxyl group HO-X, to prepare a diorganophosphorus halide, and, by reacting further with one equivalent of a compound containing one hydroxyl group HO-Y, to finally prepare an asymmetric triorganophosphite. In the preparation of asymmetric phosphonites, an analogous procedure according to the formulae v and vi may be employed.

$$\underset{(6)}{\overset{Hal}{\underset{W}{\overset{|}{P}}}}_{Hal} + HO-X \longrightarrow \underset{(4')}{\overset{O^{\nearrow X}}{\underset{W}{\overset{|}{P}}}}_{Hal} \quad (v)$$

$$(4') + HO\text{-}Y \longrightarrow W\text{-}\underset{\underset{O_{\diagdown}Y}{|}}{\overset{O^{\diagup X}}{P}} \qquad (vi)$$

$$(5)$$
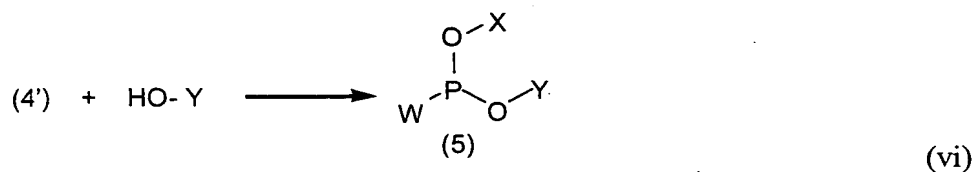
In the following formulae **vii** and **viii**, the inventive stepwise preparation of a diphosphorus compound which has a structural unit **S** (the special case of the structural unit **T** is illustrated by w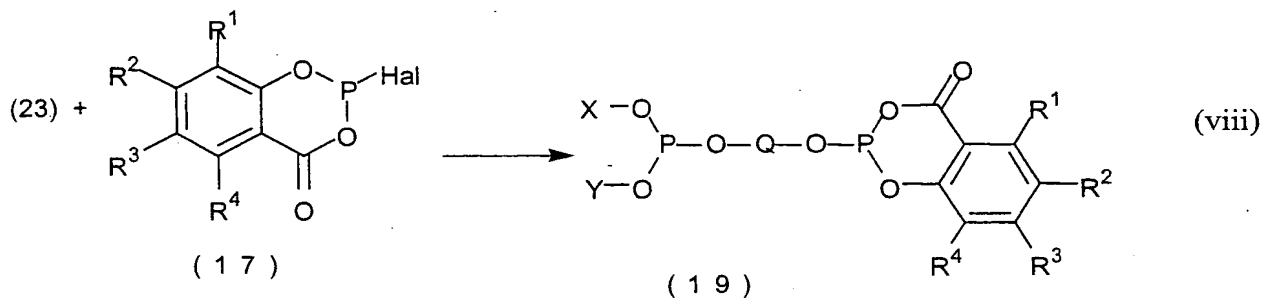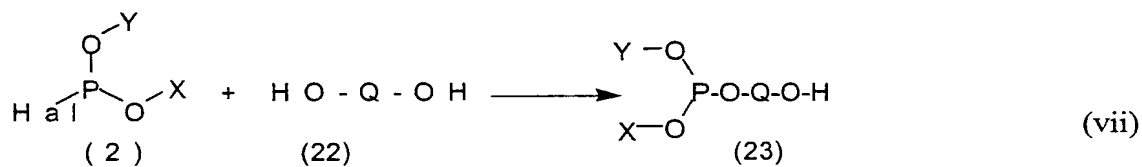ay of example) is shown using the example of a bisphosphite **10**. A dihydroxyl compound **22** is reacted with one equivalent of a halodiorganophosphite **2** to give the compound **23** which is finally reacted with a comppound **17** which has the structural unit **S** or **T** to give the bisphosphite **10**. The halodiorganophosphites mentioned may be the same or different, so that symmetric or asymmetric bisphosphites are obtained.

$$\text{Hal}\overset{O^{\diagup Y}}{\underset{O^{\diagdown}X}{P}} + H\,O\text{-}Q\text{-}O\,H \longrightarrow \underset{X\text{—}O}{\overset{Y\text{—}O}{P}}\text{-}O\text{-}Q\text{-}O\text{-}H \qquad (vii)$$

$$(2) \qquad\qquad (22) \qquad\qquad\qquad (23)$$

$$(23) + (17) \qquad \longrightarrow \qquad (19) \qquad (viii)$$

(17)

(19)

In the formulae **ii** to **viii**, X, Y and Q are each as defined above.

According to the formula **vii**, dihydroxyl compounds **22** may be reacted with diorganophosphites **2**, halodiorganophosphonites **4** or **7**, haloorganophosphinites **9**. In the second reaction step **viii**, the compounds obtained by **vii** may be reacted with a compound having the structural unit **S** or **T**. In two reaction steps, asymmetric diphosphorus compounds of the formulae **19, 20** and **21** may thus be prepared. The compound **17** used in step **viii** (bicyclic phosphochloridite) may be obtained by reacting (condensing) the compound **S'** or **T'** (a 2-hydroxybenzoic acid derivative) with a compound **0**. By directly reacting k equivalents of

the compound **17** with one equivalent of a compound Q', it is possible to prepare compounds of the formula **10** or **11** where k is the number of OH groups in the compound Q', and, to prepare the compound **11**, the compound Q' has a number k of acid groups. Preference is given in turn to carrying out all reactions steps in the presence of a basic ion exchanger.

In the case of the same organophosphorus halides, the preparation of the symmetric diphosphorus compounds, for example specific compounds of the formulae **10** and **11**, may of course be effected in one process step. When the reactivities of the two organophosphorus halides toward dihydroxyl compounds **22** are sufficiently different, the preparation of asymmetric diphosphorus compounds may likewise be carried out in one process step. Otherwise, one process step has to be provided for each reaction step.

In a similar manner to the reactions **vii** and **viii**, compounds which bear more than two phosphorus units may be prepared by reacting compounds which have three or more hydroxyl groups stepwise with organophosphorus halides.

When a compound which still contains one or more hydroxyl groups, for example a compound of the structure **24**

(24)

,
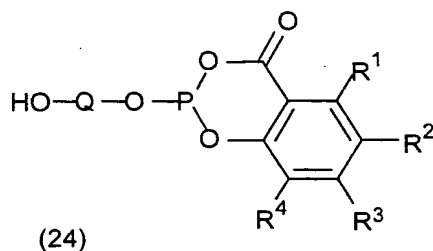
is the target of the preparation, the reaction sequence may be terminated at this stage after the reaction of a compound of the formula **17** with a compound of the formula **22**. Complete conversion of the hydroxyl groups is not necessary.

The reaction steps illustrated in reaction schemes **ii** to **viii** may be carried out batchwise. In this case, one coupling component is initially charged together with one or more ion exchange resins and the second coupling component is subsequently metered in. The feed of the components or feed of solvent may be used in some cases to control the heat production rate or the temperature in the reaction mixture. In the batchwise method, it is important for a very high

yield of desired product to initially charge and meter in the correct coupling component. For example, in the case of the selective preparation of asymmetric organophosphorus compounds of the formulae **1, 2, 3, 4, 5** or **6** according to schemes **ii** to **vi**, preference is given to initially charging the phosphorus compound, i.e. the phosphorus halide or the organophosphorus halide

5   together with one or more basic ion exchange resins and subsequently metering in the compound having an OH group (hydroxyl component). In the case of the selective preparation of asymmetric diphosphorus compounds according to schemes **vii** and **viii**, preference is given to initially charging the component having OH groups together with one or more ion exchange resins and subsequently metering in the organophosphorus halides.

10

After each process step, but also after each reaction step, the crude product may be worked up and reacted further in the next reaction step. However, it may also be more advantageous, after the complete conversion of one coupling component, to directly add the next component and to dispense with the workup between the two reaction steps. In the context of the present

15   invention, the reaction of in each case one phosphorus-halogen bond with one hydroxyl group should be regarded as one reaction step.

The reaction time in the individual reaction steps may be the same or different, but in each case sufficiently long in order to achieve the desired conversion. The reaction temperatures in the

20   individual reaction steps may be the same or different. The basic ion exchange resin or resins used in the individual reaction steps may be the same or different.

The reactors used for batchwise reaction control may be stirred tanks. The basic ion exchange resin or resins may be used in the reaction mixture as freely mobile beads. It is also possible to

25   combine the ion exchange resin or resins in the form of packages to which the convection stream of the stirrer flows. It is likewise possible to use spinning basket stirrers. In addition, the reactor systems used may be stirred reactors having full recycling (loop reactors). The flow to the ion exchange resin bed may be from above or below.

30   In another preferred embodiment of the process according to the invention, the reaction steps shown in the schemes **ii** to **viii** may also be carried out continuously in reaction spaces connected in series. Such a reaction sequence is illustrated in fig. 1: The reactant **A** and the first

coupling component **K1** are conducted into a first reaction stage **I**. The effluent of the first reaction stage **B** is subsequently, like a second coupling component **K2** too, conducted into a second reaction stage **II**. It is also possible that the coupling components **K** mentioned are effluents of one continuous, or of a plurality of continuous, reactors which are optionally

5   connected in series, i.e. are reactor sequences of the type outlined in Fig. 2 in parallel and converging connection.

In order to achieve a very high yield of the desired product in the preparation of asymmetric products, the concentration ratio of the reactants is to be appropriately set in each stage by the

10   ratios of the particular feeds. Typically, equimolar or approximately equimolar amounts are set. In the preparation of symmetric diphosphites which have an acylphosphite unit (T) or a structural unit S, it has been found to be advantageous when the molar ratio of acylphosphorus halide compound to dihydroxy compound is set to from 1:1 to 1.2:1.

15   The residence time of the reactants in the individual reaction steps may also be the same or different in the continuous mode, but in each case sufficient in order to achieve the desired conversion in the particular stage. The basic ion exchange resin or resins used in the individual reaction steps may be the same or different.

20   The reactors used for continuous reaction control may be continuous stirred tanks. The basic ion exchange resin or resins may be used in the reaction mixture as freely mobile beads. It is also possible to combine the ion exchange resin or resins in the form of packages to which the convection stream of the stirrer flows. It is likewise possible to use spinning basket stirrers. In addition, tubular reactors may be used. The flow to the ion exchange resin bed may be from

25   above or below. In the continuous reactors, partial recycling of the reactor effluents may be advantageous. In the case of the arrangement of continuous reactors in a reactor battery, the recycled fraction of the effluent of one reaction stage may be partly or fully recycled into the same stage, partly or fully conducted to the start of the preceding stage or partly or fully conducted to the start of the first stage of the first reactor of the reactor battery.

30

Quite generally, and irrespective of whether the process is carried out continuously or batchwise, when a plurality of reaction steps is carried out, identical or different ion exchangers

may be used in the reaction steps. Equally, when a plurality of reaction steps is carried out, identical or different temperatures may be set in the reaction steps. The temperature selected in the reaction stages depends substantially upon the reactivity of the feedstocks and may, within a sequence of reactors, be the same or different. The temperature is preferably increased within a

5   reactor battery. The reaction temperatures are preferably from −50°C to 150°C, preferably from −10°C to 120°C and more preferably from 20°C to 100°C. As already described, the temperature may be controlled by the feed control of the components. It is equally possible to keep the temperature at a certain temperature by the use of heatable/coolable reactors. It is also possible to combine both measures for temperature regulation. In this way, quasi-isothermal

10   operation of the entire process or of individual process or reaction steps is possible, which makes possible particularly exact setting to the optimum reaction temperature which can lead to better yields.

The process according to the invention is preferably carried out in the presence of a solvent or

15   of a plurality of solvents. The selection of the solvent depends upon the solubility of the feedstocks. In addition, the solvent has to be substantially inert toward the feedstocks under the reaction conditions. The solvent may also be added to the reaction mixture to control the temperature. Preference is given to using solvents which may function as proton carriers.

20   Preferred solvents are, for example, aromatics such as benzene, chlorobenzene, toluene or xylenes, open-chain or cyclic alkanes such as pentane, n-hexane, n-heptane, cyclohexane or methylcyclohexane, open-chain or cyclic ethers such as diethyl ether, diisopropyl ether, methyl tert-butyl ether, anisole, tetrahydrofuran, 1,4-dioxane, 1,3-dioxolane, esters such as ethyl acetate, isobutyl acetate, tert-butyl acetate, cyclic carbonic esters such as ethylene carbonate,

25   propylene carbonate and 1,2-butylene carbonate, ketones such as acetone, 2-butanone, 3,3-dimethyl-2-butanone, aromatic and aliphatic nitriles such as benzonitrile, propionitrile and acetonitrile, lactones, pyrrolidones, e.g. N-methylpyrrolidone, formamides, e.g. dimethylformamide, sulfoxides, e.g. dimethyl sulfoxide, and also N-alkylmorpholines, pyridines, quinolines, nitrogen bases such as amines and sulfolane. It is of course also possible

30   to use mixtures of these solvents.

A particularly preferred embodiment of the process according to the invention is carried out in

the presence of a proton transferrer which is preferably present in homogeneous form in the reaction mixture or reaction solution. The proton transferrers used may be bases which are weaker bases than the weakly basic ion exchangers. The proton transferrers used are preferably those compounds which, in addition to the function as a proton transferrer, may also assume

5   the function of the solvent. Such compounds may be, for example, N-methylpyrrolidone or methylimidazole. The use of a proton transferrer which is homogeneously distributed in the reaction mixture may increase the reaction rate, since the reaction is promoted by the reactants no longer having to come into contact directly with the ion exchanger, but rather only with the weaker base which is, though, homogeneously distributed in the reaction mixture. The proton

10   transferrer then reacts further with the ion exchanger, but serves only as a transferrer. In the reaction mixture, there is preferably a molar ratio of proton transferrer to the free base provided by the ion exchanger of from 0.0001:1 to 1:1, preferably from 0.001 to 0.01.

Preference is given to carrying out the process according to the invention in the presence of one

15   or more polymeric, (weakly) basic ion exchange resins, preferably based on styrene-divinylbenzene copolymers, in order to scavenge the hydrogen halide formed in the condensation of phosphorus trihalides or organophosphorus halides with organic compounds bearing hydroxyl groups. Particular preference is given to using ion exchange resins based on styrene-divinylbenzene copolymers which bear N,N-dialkylamine groups, for example N,N-

20   dimethylamino groups. It is possible to use macroreticular ion exchange resins or those of the gel type. Particular preference is given to using macroreticular ion exchange resins.

Very suitable for use in the process according to the invention are commercially available (weakly) basic ion exchange resins, for example Lewatit MP62, DOWEX M-43 or Amberlyst

25   A21.

Preference is given to using the ion exchanger in the form of particles, preferably having an average particle size of from 10 μm to 2 mm, more preferably from 0.1 to 1.5 mm, or in the form of a fixed package. In this way, it is ensured that the ion exchanger can be very simply

30   removed from the reaction mixture or separated from it.

In the process according to the invention, at least sufficient (weakly) basic ion exchanger is

used that for each mole of acid which is released in the compound formation or formations, at least one mole of free base is available on the ion exchanger. Preference is given to using sufficient ion exchanger that the ratio of moles of acid resulting from the release to moles of free base released by the ion exchanger is from 1:1 to 3:1, preferably from 1.1:1 to 2:1.

5

Before it is used in the process according to the invention, the ion exchange resin is preferably dried by known techniques, for example by heat treatment under reduced pressure (G. Mohorcic, M. Pregelj, M. Pirs, Ion Exchange and Membranes (1975), 2(2), 107 − 110, C. Buttersack, K. Struss, H. Widdecke, J. Klein, Reactive Polymers, Ion Exchangers, Sorbents

10 (1987), 5(2), 171 - 180) or by azeotropic distillation with suitable azeotroping agents (GB 1120402).

To carry out the process in continuous or quasi-continuous mode, at least two parallel reactors are provided per reaction step or process step and are connected in such a way that when the

15 ion exchanger is exchanged, regenerated or dried in one of the reactors, the reaction can be continued in the other reactor.

In order to the keep the costs of the process low, it is appropriate to regenerate the ion exchange resin laden with hydrogen halide (to bring it into the basic form) and reuse it.

20

Weakly basic ion exchangers are regenerated typically with NH_4OH, Na_2CO_3 or $NaOH$. Precise instructions on this subject are provided by manufacturer's technical information sheets (for example Lewatit-Selective ion exchangers, Instructions for laboratory trials with Lewatit selective ion exchange resins, Technical Information, Bayer; Dow Liquid Separations, Dowex

25 Marathon WBA, Ion Exchange Resin, Engineering Information, The Dow Chemical Company; Dowex Ion Exchange Resins, Properties, Impurities and Concentrations of Regenerant Chemicals).

Further information on the regeneration of ion exchangers can be found, for example, in:

30 Regeneration of Anion Exchange Resins with Regular-Grade Diaphragm-Cell Caustic Soda: A Five-Year Plant Trial (IWC Proceedings, 10(88, S.D. Coker, M.P. Murphy); Petrochemical Company Anion Exchange Resin Regeneration Trial (Dow Report, 8/89, Michael A. Smith)

and Caustic Soda for Ion Exchange Resin Regeneration (Marketing Research Report, 4/86, Ralph A. Bacon).

The present invention is illustrated in detail with reference to the figures fig. 1 and fig. 2
5   without the invention, whose scope of application is evident from the description and the claims, being restricted to these embodiments.

Fig. 1 shows one possible connection of reactors for a continuous mode. The process of fig. 1 has three reaction steps. In the first step, a reactant **A**, for example a phosphorus trichloride, is
10   fed into a reactor **I** which has an ion exchanger. Component **K1** which is a first compound having an OH group is likewise metered into this reactor. The amount of component **K1** is preferably such that there is a molar ratio of **A** to **K1** of 3:1. The monoorganophosphorus dichloride obtained as the product **B** of the first reaction step **I** is transferred to the reactor **II** of the next reaction step which likewise has an ion exchanger. Also metered into this reactor is the
15   component **K2** which is a second compound having an OH group. The amount of component **K2** is preferably in turn such that there is a molar ratio of **B** to **K2** of 2:1 on entry into the reactor. The diorganophosphorus chloride obtained as the product **C** of the second reaction step **II** is transferred to the reactor **III** of the next reaction step which likewise has a basic ion exchanger. Also metered into this reactor is the component **K3** which is a third compound
20   having an OH group, for example a compound of the formula 24. The amount of component **K3** is preferably such that there is a ratio of **C** to **K3** of 1:1 on entry into the reactor. The product **D** obtained from reactor **III** is in the present case a phosphite which has a structrual unit **T**.

25   Fig. 2 shows another possible connection of reactors in which one process variant of the process according to the invention which has a plurality of reaction steps can be carried out continuously. Thus, the reactant A_1, for example a halodiorganophosphite of the formula 2, is fed together with the component **K1**, for example a dihydroxyl compound of the formula 22, in a ratio of 1:1, into reactor I_1 which has an ion exchanger. The reaction product B_1 obtained is a
30   product of the formula 23. The reactant A_2, for example a compound of the formula **O**, is fed together with the component **K2**, for example a 2-hydroxybenzoic acid derivative **T'** in a ratio of 1:1, into reactor I_2 which likewise has an ion exchanger. The reaction product B_2 obtained is

a product of the formula **17**. The products B_1 and B_2 are conducted together, preferably in a molar ratio of 1:1, into the reactor **II** which likewise has a basic ion exchanger. In this reactor, the products B_1 and B_2 react to give product **C** of the formula **19** with elimination of hydrogen chloride.

5

The examples which follow are intended exclusively to illustrate the invention but not restrict its scope of application which is evident exclusively from the description and the claims.

Examples:

10   All preparations were carried out under protective gas using standard Schlenk techniques. The solvents were dried before use over suitable desiccants. The ion exchanger used, Lewatit MP-62, was suspended in hexane to remove water and the water was removed azeotropically in a Dean-Stark apparatus.

15   **Example 1: Preparation of 3-chloro-2,4-dioxa-3-phospha-phenanthren-1-one or 2-chloro-4H-naphtho[1,2-d]-1,3,2-dioxaphosphorine-4-one of the formula I**
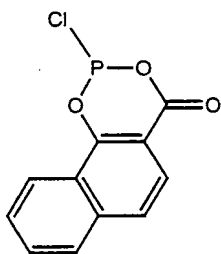

I

20   **Example 1.1: inventive, using an ion exchanger**

A mixture of 9.5 g (0.05 mol) of 1-hydroxy-2-naphthoic acid and 58 g (approx. 0.1 mol) of Lewatit MP 62 ion exchanger and 250 ml of toluene was stirred vigorously for 30 min, in the course of which the acid is gradually dissolved. Subsequently, a solution of 4.4 ml = 6.9 g (0.05 mol) of phosphorus trichloride in 30 ml of toluene was added dropwise at room

25   temperature, in the course of which gentle heat evolution took place. For workup, the solution was decanted from the ion exchanger, the residue was washed twice with approx. 80 ml of dried toluene and the solvent (toluene) was removed in an oil-pump vacuum. The product obtained was a colorless solid. The yield was 75% of theory.

Example 1.2: Comparative example, reaction in the presence of triethylamine.

To a suspension of 18.82 g (0.1 mol) of 1-hydroxynaphthoic acid in 200 ml toluene was slowly added dropwise at 0°C a solution of 42.2 ml (30.7 g; 0.3 mol) of triethylamine and 8.8 ml

5   (13.9 g; 0.1 mol) of phosphorus trichloride in 30 ml of toluene, and the mixture was subsequently stirred. A colorless precipitate (amine hydrochloride) formed which complicated the stirring and subsequently made it impossible. Even addition of 100 ml of dried toluene could not make the suspension stirrable again. Subsequently, the reaction mixture was warmed to room temperature and left to react overnight. Afterward, the colorless solid was filtered off

10   and washed 2 x with 100 ml of toluene. The resulting clear solution was freed of volatile constituents in an oil-pump vacuum, and an oily residue was obtained. The crude product was dissolved again in toluene, and the precipitation of a colorless solid was observed. After repeated filtration, 18.6 g of a colorless solid were obtained. Yield: 74.35%.

15   For the same yield, the process according to the invention allows complicated removal of the base to be dispensed with. In addition, the process according to the invention succeeds in removing the base quantitatively, so that no traces of the base which could disrupt subsequent reactions are present.

20   **Example 2: Preparation of 2-chloro-2,3-dioxa-2-phosphanaphthalin-4-one of the formula II**

II
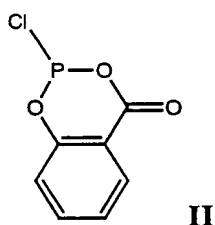
Example 2.1: inventive, using an ion exchanger

25   To a mixture of 1.38 g (0.01 mol) of salicylic acid and 11.7 g of MP62 Lewatit in 20 ml of toluene are added dropwise at room temperature 1.375 g (0.01 mol) of phosphorus trichloride. The reaction mixture is stirred for 15 min. A GC-MS investigation of the reaction solution shows complete conversion of the salicylic acid, and the desired product is formed with 100%

selectivity.

**Example 2.2: comparative example with triethylamine**

In a comparative experiment according to example 2.1 in which 0.02 mol of triethylamine was used instead of ion exchanger as a base, only 37% product formation was observed in the reaction under room temperature conditions. In addition, three further products which were not more precisely identified were formed.

Prior Art:

In **Reaction product of phosphorus trichloride with salicylic acid; Cade, J. A.; Gerrard, W.** *Chemistry & Industry* **1954**, 402, the preparation of 2-chloro-4H-1,3,2-benzodioxaphosphorin-4-one with a yield of 85% is described, by reacting 1 mol of PCl_3, 1 mol of salicylic acid and 1 mol of pyridine in diethyl ether at − 10 °C.

In **An examination of the reaction between phosphorus trichloride and salicylic acid.** Young, Richard W., *Journal of the American Chemical Society* **1952**, *74*, 1672-3, 138 g of salicylic acid, 150 g of PCl_3 and 150 ml of toluene are boiled to reflux for 3 h, the toluene and PCl_3 are subsequently removed under reduced pressure and the residue is distilled. 120 g of 2-chloro-5,6-benzo-1,3,2-dioxaphosphorin-4-one were obtained, which corresponds to a yield of 59%.

It can easily be seen that the use of the weakly basic ion exchanger as a base enables a selectivity of 100%, which is enabled by none of the other processes.

Example 3: Phosphite of the formula III, prepared from 2,2'-bis(6-tert-butyl-1-hydroxy-4-methoxyphenyl) and phosphorus trichloride
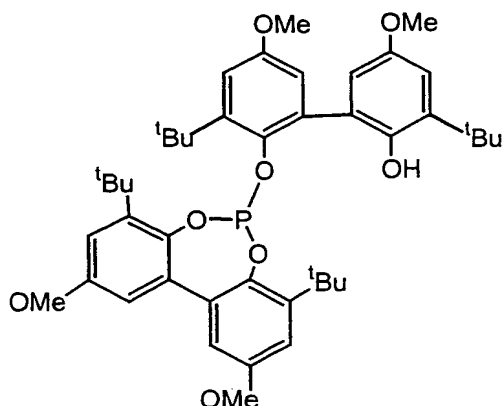
III

Example 3.1: inventive

To a mixture of 26.5 g (0.045 molar eq.) of Lewatit MP-62 ion exchanger and 1.3 ml (2 g;

5   0.015 mol) of phosphorus trichloride in 200 ml of toluene was added dropwise with vigorous

stirring at room temperature a solution of 12.3 g (0.03 mol) of 2,2'-bis(6-tert-butyl-1-hydroxy-

4-methoxyphenyl) in 100 ml of toluene. Subsequently, the reaction mixture was heated to 60°C

for 2 h and cooled overnight. For workup, the ion exchanger was filtered off by means of a

glass frit and washed 4 times with 50 ml of toluene. The solution was freed of volatile

10   constituents at room temperature in an oil-pump vacuum, and the product was dried under

reduced pressure. Yield: 11.8 g, corresponding to 93% of theory.

Example 3.2: Prior Art according to EP 1 201 675

To a solution of 2.42 g of 2,2'-bis(6-tert-butyl-1-hydroxy-4-methoxyphenyl) (6.75 mmol) and

15   1.6 ml of pyridine in 22 ml of THF is added dropwise at 0°C a solution of 0.93 g of PCl₃

(6.75 mmol) in 10 ml of THF. After stirring at 25°C for 4 h, the solvent is removed under

reduced pressure. After adding 40 ml of diethyl ether, filtering and concentrating under reduced

pressure, 2.8 g (98%) of spectroscopically pure chlorophosphorous ester of 2,2'-bis(6-tert-

butyl-1-hydroxy-4-methoxyphenyl) are obtained. 2.8 g of this chloroester (6.62 mmol) in 20 ml

20   of THF are added at room temperature to a monolithium phenoxide solution, obtained at -20°C,

from 2.37 g of 2,2'-bis(6-tert-butyl-1-hydroxy-4-methoxyphenyl) (6.62 mmol) in 30 ml of THF

and 20.7 ml of 0.32 M hexane solution of n-butyllithium (6.62 mmol). After 24 h, the mixture

is concentrated under reduced pressure. Addition of 40 ml of methylene chloride, filtration and

removal of the solvent under reduced pressure give 4.6 g (93%) of highly viscous product.

25   **Use of triethylamine as described in the prior art (EP 0 213 639).**

Approx. 179.2 g (0.5 mol) of 2,2'-dihydroxy-3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl are added to approx. 1600 ml of toluene. Sufficient toluene was then removed azeotropically in order to remove traces of moisture. The diol-toluene solution was then cooled to 80°C and approx. 168.7 g (1.67 mol) of triethylamine were added.. Approx. 68.7 g (0.5 mol) of PCl_3

5   were added to 200 ml of toluene. To this solution was added dropwise at -10°C within 1 h and 40 min a diol-toluene solution. The reaction solution was kept at this temperature for a further 30 min. Subsequently, the solution was allowed to warm to room temperature within 2 h. Subsequently, the reaction mixture was filtered to remove the triethylamine hydrochloride precipitate and the precipitate was washed twice with 200 ml of toluene. The filtrate and the

10 wash liquor were combined to give 717.5 g of solution of the phosphoochloridite intermediate in toluene.

Approx. 170 g of further 2,2'-dihydroxy-3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl were added to 800 ml of toluene. Subsequently, 48.1 g of triethylamine were added. The 717.5 g of

15 the abovementioned phosphorochloridite-toluene solution were added to this solution at room temperature within 45 min. The temperature was increased to 80°C for one hour and 45 minutes and then to 95°C for 2 hours. Subsequently, the mixture was cooled to room temperature. Approx. 600 ml of distilled water were added to the reaction mixture in order to dissolve the solid triethylamine hydrochloride. After the solution had been given time to settle,

20 the phases which formed were separated. The aqueous phase was extracted twice with 250 ml of toluene. The organic phase and the extracts were combined and dried over dry magnesium sulfate for one hour. Subsequently, the solution was filtered and concentrated under reduced pressure to give a solid residue. The residue was recrystallized with acetonitrile and 242.5 g (65.4 % of theory) of the diorganophosphite were obtained.

25

As can be clearly seen with reference to the inventive example, the same yield can be obtained as in the prior art process, but the process control is distinctly simpler.

Example 4: Preparation of a biphosphite of the formula IV
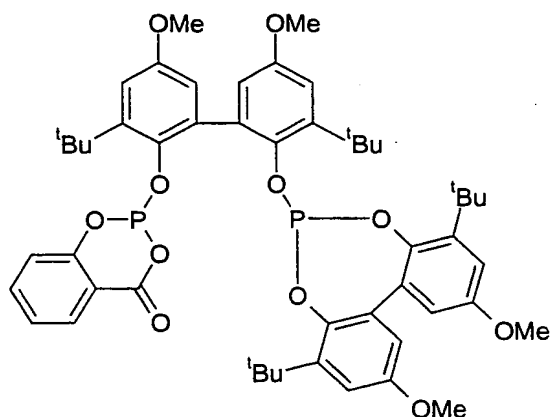
IV

Example 4.1: inventive

To a mixture of 32.4 g (0.055 mol) of MP-62 ion exchanger and 18.6 g (0.025 mol) of 2-[(3,3'-
di-tert-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl)phosphite]-2'-hydroxy-5,5'-dimethoxy-
1,1'-biphenyl **(Formula III)** in 200 ml of toluene was added dropwise a solution of 6.09 g
(0.03 mol) of 2-chloro-4H-1,3,2-benzodioxaphosphorin-4-one in 50 ml of toluene.
Subsequently, the reaction mixture was stirred at 60°C for 3 h. For workup, the ion exchanger
was filtered off, toluene removed under reduced pressure and the residue recrystallized from
acetonitrile. The yield was 61% at a purity of greater than 98%.

Example 4.2: Prior art acording to EP 1 201 675

Preparation of a compound of the formula **III**

To a solution of 2.42 g of 2,2'-bis(6-*tert*-butyl-1-hydroxy-4-methoxyphenyl) (6.75 mmol) and
1.6 ml of pyridine in 22 ml of THF is added dropwise at 0°C a solution of 0.93 g of PCl_3
(6.75 mmol) in 10 ml of THF. After stirring at 25°C for 4 h, the solvent is removed under
reduced pressure. After adding 40 ml of diethyl ether, filtering and concentrating under reduced
pressure, 2.8 g (98%) of spectroscopically pure chlorophosphorous ester of 2,2'-bis(6-*tert*-
butyl-1-hydroxy-4-methoxyphenyl) were obtained; ^{31}P NMR (CD_2Cl_2) δ 172.7 ppm. 2.8 g of
this chloroester (6.62 mmol) in 20 ml of THF are added at room temperature to monolithium
phenoxide solution, obtained at -20°C, from 2.37 g of 2,2'-bis(6-*tert*-butyl-1-hydroxy-4-
methoxyphenyl) (6.62 mmol) in 30 ml of THF and 20.7 ml of a 0.32 *M* hexane solution of
n-butyllithium (6.62 mmol). After 24 h, the mixture is concentrated under reduced pressure.
Addition of 40 ml of methylene chloride, filtration and removal of the solvent under reduced

pressure give 4.6 g (93%) of highly viscous product.

Analysis (Cal. for $C_{44}H_{57}O_8P$ = 744.9 g/ Mol) C 70.35 (70.95); H 7.86 (7.71). ^{31}P NMR (CD_2Cl_2) δ 140.7 ppm. ^{1}H NMR (CD_2Cl_2) δ 1.43 (s, 9 H); 1.56 (s, 9 H); 1.63 (s, 9 H); 1.67 (s, 9 H); 4.01 (s, 3 H);4.03 (s, 6 H); 4.05 (s, 3 H); 5.42 (s, 1 H); 6.7...7.3 (m, 8 H) ppm. FAB MS:

5   *m/e* 745 (37%, *M*[+]); 387 (100%, *M*[+]- 2,2'-bis(6-*tert*-butyl-1-hydroxy-4-methoxyphenyl)). IR ($CHCl_3$, 0.1 mm CaF_2), ν (OH) = 3549 cm^{-1}.

Preparation of the compound of the formula IV

To a solution of 2.27 g of the compound of the formula **III** (9.19 mmol) in 72.5 ml of THF

10   were added dropwise at -20°C with stirring within 10 min 28.7 ml of a 0.32 molar solution of n-butyllithium (3.04 mmol). After warming to room temperature, the mixture is initially stirred for 30 min, and the resulting mixture is then added to 66.5 ml of a 0.138 molar solution of 2-chloro-1,3-dioxa-2-phosphanaphthalen-4-one (3.04 mmol) (Formula **II** prepared according to example 2) in THF. The reaction mixture was stirred at 25°C for 4 h, the solvent was removed

15   under reduced pressure and the syrup-like residue was stirred with 60 ml of hexane for 2 h. The mixture was filtered and washed twice with 7 ml of hexane, and the filtercake was extracted with hot hexane and with diethyl ether. After reducing the amount of solvent to one third and subsequently storing the solution at -20°C, the product is obtained in a 54% yield. ^{31}P NMR (CD_2Cl_2): 119.2 (m); 119.8 (m); 139.5 (m); 140.1 (m); ^{1}H NMR (CD_2Cl_2): 1.02..1.26 (36 H);

20   3.67..3.74 (12 H); 6.43..7.99 (12 H). FAB-MS: m/e 911 (100%, M+), 744 (18%), 387 (13%).

As can be seen clearly with reference to example 4, the process according to the invention achieves distinctly better yields.